A STUDY OF IONIZATION IN CYANOGEN FLAMES AT REDUCED PRESSURES BY THE CYCLOTRON RESONANCE METHOD

E. M. BULEWICZ AND P. J. PADLEY

The ionization in the reaction zone of cyanogen–oxygen flames at reduced pressure was studied by the method of cyclotron resonance. Although the temperatures of these flames are sufficiently high for thermal ionization of nitric oxide to account for the observed free electron concentrations, other characteristics of the ionization are consistent only with the operation of nonthermal processes. These processes, however, appear to be different from those inferred to be taking place in hydrocarbon–oxygen flames, and seem to involve energetic three-body reactions. Some auxiliary spectral evidence is also presented.

When traces of hydrogen are added, the electron concentration decreases considerably—particularly for fuel-lean flames. As the concentration of cyanogen in the fuel is reduced to about 20 per cent, a second ionization maximum appears, associated with a greenish glow from the burned gases. It is shown that attempts to explain this effect simply in terms of reactions occurring in hydrocarbon–oxygen flames meet with difficulties which cannot be resolved at this stage.

Introduction

In spite of the potentialities of the cyanogen flame as a high energy spectroscopic source[1] (calculated maximum temperature about 4800°K), the fuel has so far received comparatively little attention. A study of the spectroscopy of the cyanogen–oxygen flame was made by Thomas, Gaydon, and Brewer,[2] but the few kinetic data so far available have been obtained in lower temperature, static systems.[3,4] CN and CN intermediates are frequently found in other gas reactions, e.g., when active nitrogen and other gas discharge products react with hydrocarbons, carbon monoxide, and carbon dioxide.[5-7] Apart from mass spectrometric observations carried out by van Tiggelen,[8] ionization processes appear not to have been studied at all.

The most easily ionizable component of cyanogen flame gases is NO (I.P. = 9.25 ev).[9] In fuel-rich flames at thermodynamic equilibrium, calculated [NO] is low—not greater than 10^{-2} per cent of the total gases (using equilibrium constants from Gaydon and Wolfhard[10] and an estimated flame temperature of 4000°K). In lean flames, however, [NO] can be of the order of 1 per cent of the burned gases. Thus, if the ionization is thermal, and if the Saha equation can be applied, a concentration of free electrons in the range 10^{10}–10^{11} electrons/cc is expected at the pressures (approx. 0.1 atmospheres) used in this study. Such concentrations should be readily detectable by the cyclotron resonance method.

Experimental

The cyclotron resonance method of measurement of free electron concentrations and of electron–molecule collision cross sections in burned flame gases under a variety of conditions has been described in earlier papers[11,12] and elsewhere at this symposium.[13]

A simple quarter-plate Hilger spectrograph was used to investigate qualitatively some of the spectral features of the flames under the same conditions as when the electron concentrations were measured. Photographs were taken on Kodak 103a–O and F plates. The emission was studied both in the reaction zone and in the burned gases; for this purpose the reaction vessel was fitted with plane quartz windows. A small grating monochromator was also used for visual observations.

Cyanogen was obtained from the American Cyanamid Co. It was prepared by the high temperature reaction of hydrogen cyanide and chlorine; drying of the gas was therefore considered unnecessary. Its toxicity only occasionally proved troublesome, as the flames were burned in a closed system and the components of the burned gases not removed by the pump traps were piped directly out of the building. Since the flame was not in direct contact with the vessel

walls, air-cooled Pyrex vessels used in previous studies were found to be adequate here. The flames were burned in the pressure range 50–200 mm Hg, above Pyrex tubes 10–15 mm in diameter. Measurements were made in the reaction zone, at the position of maximum attenuation, unless otherwise stated.

Results and Discussion

Cyanogen–Oxygen Flames

Electron Concentration and Electron–Molecule Collision Cross Section as a Function of Flame Composition. A typical cyclotron resonance line for a C_2N_2-O_2 flame at 60 mm Hg is shown in Fig. 1, with a line for a C_2H_2-O_2 flame at 10 mm Hg included for comparison. (The cause of the slight asymmetry of the lines is discussed elsewhere.[12])

It has been shown[13] that the observed cyclotron resonance line width, ΔH, in gauss, is related to the average electron molecule collision cross section Q and the total pressure p in mm Hg by the equation

$$\Delta H/p = 6.8 \times 10^{17} \times Q/T^{\frac{1}{2}}.$$

Allowing for the pressure difference between the two flames and for the fact that the temperatures of the cyanogen and acetylene flames were about 4000°K and 2000°K, respectively, it can be seen that if the average electron–molecule collision cross section were the same in both cases, the
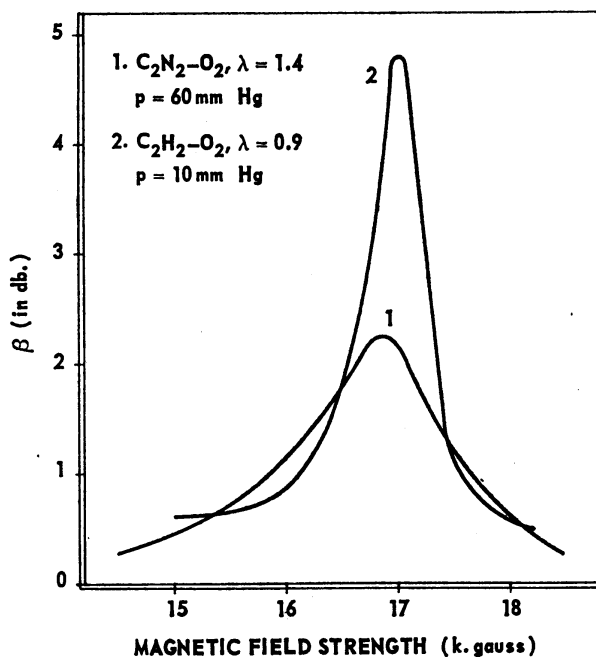
Fig. 2. Variation of $\Delta H/p$ with λ.

cyanogen line would be expected to be wider than observed by at least a factor of two. Evidently the average Q for cyanogen flames is considerably lower than the value of about 40 Å^2 found for near stoichiometric acetylene flames, due probably to the absence of H_2O from the burned gases for which $Q \simeq 80$ Å^2 under these conditions.[11]

The variation of $\Delta H/p$ with λ {λ being defined as ([O_2] unburned)/([O_2] required for combustion to carbon monoxide and nitrogen)} is shown in Fig. 2. Absolute values of Q cannot be given since the temperatures of the flames have not been measured.

The electron concentration, n, is related to ΔH, (defined above) the attenuation at the center of the line, β (in db) and the thickness of the flame, d (in cm), by the expression[13]

$$n = \Delta H\beta/40\pi ed \; \log_{10} e = 3.87 \times 10^7 \; \Delta H\beta/d.$$

The flame described in Fig. 1, for which β, ΔH, and d were about 2.3 db, 1500 gauss, and 1.5 cm, respectively, contained close to 10^{11} electrons/cc, which is very similar to the electron concentration found in acetylene flames at about 15 mm Hg.

Fig. 1. Typical cyclotron resonance absorption lines: curve 1, C_2N_2-O_2, $\lambda = 1.4$, $p = 60$ mm Hg; curve 2, C_2H_2-O_2, $\lambda = 0.9$, $p = 10$ mm Hg.
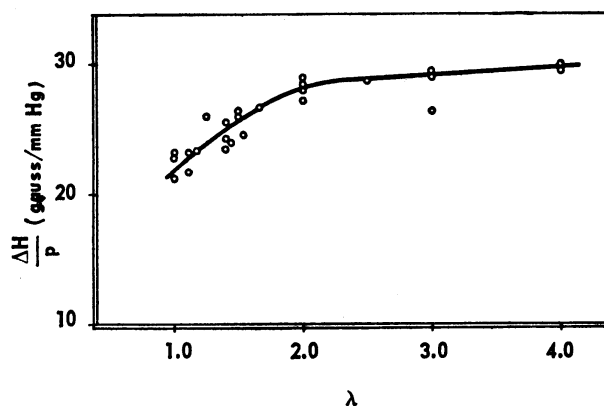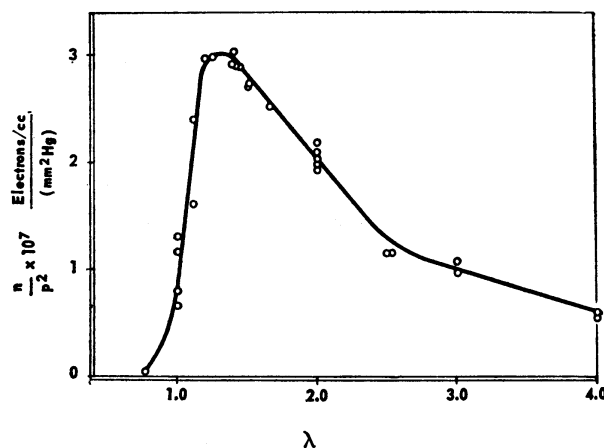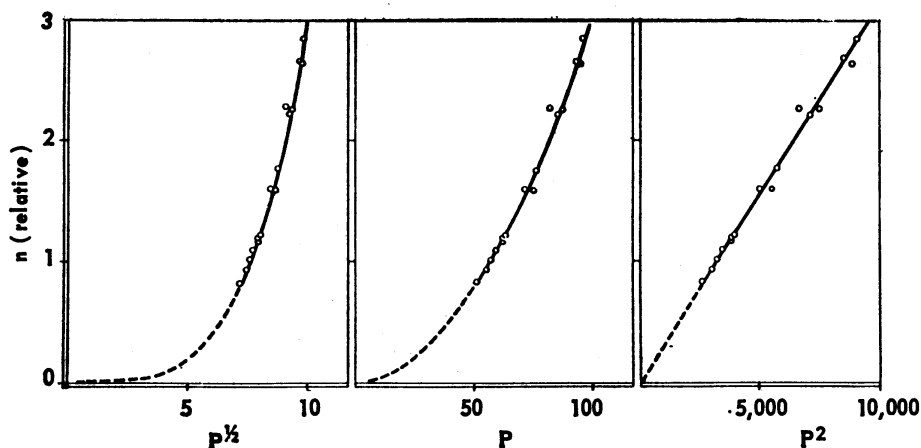
Fig. 3. Variation of n/p^2 with λ.

FIG. 4. Plots of n as a function of $p^{\frac{1}{2}}$, p, and p^2. p in mm Hg.

The dependence of the ionization on the flame composition is illustrated in Fig. 3, where n/p^2 has been plotted against λ (this type of plot was chosen for reasons to be discussed shortly). The sharp drop of n/p^2 on the fuel-rich side is not a result of the presence of several per cent of the electron acceptor CN, for even at a flame temperature as low as 3000°K, the formation of CN^- will reduce n by not more than about 20 per cent.[14] The only positive ion associated with the free electrons[8] is NO^+, contrasting sharply with the complexity of the ion spectra of hydrocarbon flames, in which H_3O^+, various hydrocarbon fragments and other ions appear.[15–17]

Since the temperatures of the flames used were not known (an attempt at measuring them, using a modification of the line reversal method[18] is to be made shortly), the equilibrium concentrations of all the species present could only be approximately estimated. For temperatures in the 4000–3000°K range, however, the ionization expected on the basis of equilibrium is comparable to that observed; in hydrocarbon flames, on the other hand, the ionization is known to be very considerably above the equilibrium level.[9] It is, therefore, of some interest to determine whether the ionization in cyanogen flames is, in fact, thermal.

On simple kinetic considerations this would seem unlikely, since it has been shown[19] that, for alkali metals, processes of the type

$$M + X \rightarrow M^+ + e + X$$

where X is a third body, require at least 1 msec for equilibration at atmospheric pressure, for activation energies greater than about 5 ev. For NO, with an ionization potential of 9.25 ev and with a binary collision frequency of about 2×10^8 sec^{-1} under flame gas conditions, it appears that the ionization could be produced in the time taken by the gases to travel through the reaction zone (ca 100 msec) only if these gases consisted of pure NO. In addition, it might be noted here that the introduction of NO into the preburned gases in quantities up to 5 per cent of the total volume has very little effect on the level of ionization other than that which can be attributed to a "dilution" effect. Thus the measured electron concentrations may be about two orders of magnitude too high.

Variation of n with Pressure. n was measured for cyanogen–oxygen mixtures burned at 50–200 mm Hg. Typical results are shown in Fig. 4 where n has been plotted against $p^{\frac{1}{2}}$, p, and p^2. If the ionization were thermal, the first plot should be a straight line. Since for cyanogen flames $n \propto p^2$, it is evident that the ionization is nonthermal, but different from that found in hydrocarbon flames for which $n \propto p$ (see Fig. 8). The quantity n/p^2 is therefore used throughout this paper in comparing ionization levels in different flames.

Ionization in Cyanogen–Oxygen Flames Containing Argon, Nitrogen, and Excess Oxygen. Figure 5 is a logarithmic plot of n/p^2 against r, where $r = [C_2N_2 + O_2]/[\text{total unburned volume}]$ for the addition of argon and nitrogen to a cyanogen flame. Reduction of r to about 0.5 results in a pressure rise from approx. 60 mm to 170 mm Hg, and an approximately threefold decrease in n, irrespective of which gas is added, although the nitrogen-containing flames are cooler than those with the same proportion of argon. Further, if r were reduced to 0.5 by nitrogen addition, an initial flame temperature of about 4500°K would fall to below 3000°K which, even neglecting any changes in [NO] would lead to at least 10^3-fold reduction in n as calculated from the Saha equation. This is about 10^2 times greater than the observed change. Thus nonthermal ionization is confirmed.
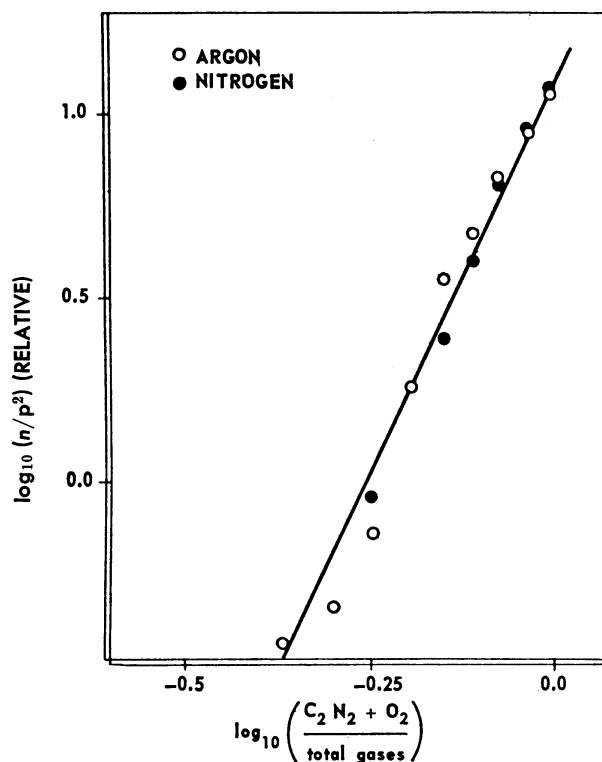
FIG. 5. Addition of argon (open circles) or nitrogen (closed circles) to a C_2N_2-O_2 (λ = 1.4) flame. (Both sets of results fall on the same line.)

The slope of the plot of Fig. 5 shows that, approximately n/p^2 appears to vary as r^4 (r is proportional to the fraction of fuel in the unburned gases)—this is true for flames with nitrogen or argon at all λ. For undiluted flames containing excess oxygen,

$$n/p^2 \propto ([C_2N_2]/[C_2N_2 + O_2])^2.$$

In contrast, for hydrocarbon flames $n/p \propto$ (fuel fraction)^2 for all flames with nitrogen, argon, or excess oxygen. This emphasizes again the marked difference between cyanogen and other fuels.

Decay of n Above the Reaction Zone. Figure 6 shows that the experimental points fit a first order decay plot reasonably well. There is slight curvature near the reaction zone itself, in the sense expected if there were some contribution from second order decay processes at very high electron concentrations.

Both Williams[20] and Calcote[21] have obtained similar plots for hydrocarbon-oxygen flames below about 30 mm Hg. Williams attributes this effect to electron attachment whereas Calcote ascribes it to ambipolar diffusion. Above about 30 mm Hg, second order recombination becomes of increasing importance in hydrocarbon-oxygen flames.[21] In cyanogen-oxygen flames, however, the present authors find that first order processes
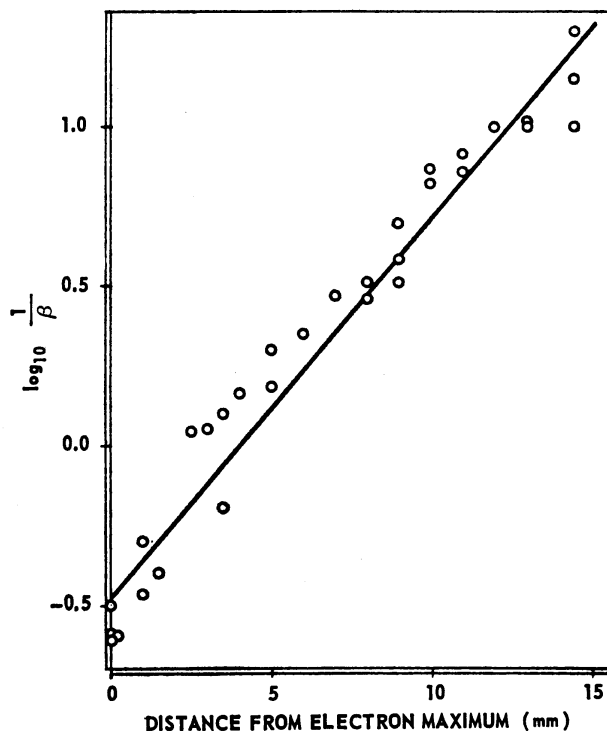

FIG. 6. Decay of ionization with time (proportional to height in the flame) after leaving the reaction zone. C_2N_2-O_2, λ = 1.25, p = 55 mm Hg.

appear to persist up to at least 100 mm Hg (the highest pressure at which such measurements were made). Interpretation of such results as favoring electron attachment as the main process of electron decay must be made with caution, however, on account of changes of flame shape and temperature over the region of measurement, and on account of the thickness (approx. 3 mm) of flame sampled.

Spectral Features of Cyanogen–Oxygen Flames. The strongest features in the reaction zone of these flames were the CN red and violet systems and the C_2 Swan system. The γ–NO system and an unidentified system[2,5] at 3250–3300 Å appeared less strongly. The β–NO system was only just detectable—at atmospheric pressure it is reported to be strong.[2] The intensities of the CN and C_2 systems are greatest in fuel-rich flames, whereas the intensities of the γ–NO and the unidentified system are at a maximum in the λ = 1.1–1.5 range. Very fuel-rich cyanogen flames are brilliant white, and deposit carbon—in contrast to acetylene flames and cyanogen flames at atmospheric pressure.[2]

In the burned gases up to about 5 cm from the reaction zone all the above features are still observed, together with a strong continuum in the blue and ultraviolet (probably mainly due to the CO + O reaction[22]) and a greenish glow, which may arise from the NO + O reaction.[22]
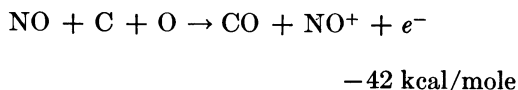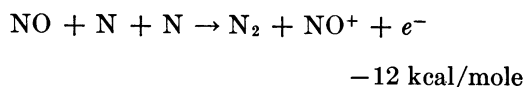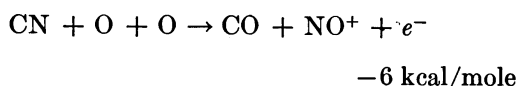
The intensity of the glow, γ–NO, and the un-identified system all vary with flame composition rather like the electron concentration.

Addition of up to 5 per cent of NO to the burned gases weakens the CN and C_2 emission, possibly through reactions of the type

$$CN + NO \rightarrow N_2 + CO \qquad -144 \text{ kcal/mole}$$

$$C_2 + NO \rightarrow CN + CO \qquad -180 \text{ kcal/mole}$$

In the absence of precise photometric data it is not possible to give an unambiguous interpretation of all the ionization phenomena described. The following suggestions are, therefore, mainly tentative.

The explanation of the pressure dependence of n most probably lies in the production of ions in a reaction of a higher kinetic order than that by which they are destroyed, since at the point of measurement (maximum electron concentration) steady state conditions are presumed to exist. The simplest reactions energetically feasible for production of NO^+ are all termolecular, viz.,

$$CN + O + O \rightarrow CO + NO^+ + e^-$$

$$-6 \text{ kcal/mole}$$

$$NO + N + N \rightarrow N_2 + NO^+ + e^-$$

$$-12 \text{ kcal/mole}$$

$$NO + C + O \rightarrow CO + NO^+ + e^-$$

$$-42 \text{ kcal/mole}$$

Of these the first could possibly proceed via CNO intermediate. The second has been proposed to explain the presence of free electrons in active nitrogen containing traces of oxygen.[23,24] The addition of NO to these flames has little effect on n, but this does not necessarily rule out the second reaction since extra NO can reduce [N] as well as produce NO^+.[25] For electron removal the simplest reaction to propose is the dissociative recombination process

$$NO^+ + e^- \rightarrow N + O$$
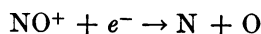
which can be up to 63 kcal/mole exothermic. This reaction has been recently shown to be the predominant process of electron decay in ionized NO.[26] The occurrence of such processes at the point of measurement in the reaction zone (where steady state conditions apply to n) would give

$$n = (k_{(A+B+C)}[A][B][C]/k_{(NO^+ + e^-)})^{\frac{1}{2}}$$

provided $[NO^+] = [e^-] = n$, and where A, B, and C represent the species involved in the ion production reaction. If [A], [B], and [C] are all proportional to (approximately) the first

power of p, then a reasonable explanation of the pressure dependence is provided.

It is perhaps of interest to note that, if the predominant process of electron removal is electron attachment to a species X, with [X] proportional to p, then

$$n = k_{(A+B+C)}/k_{(X+e^-)} \times ([A][B][C])/[X]$$

and thus an exact fit with the observed pressure dependence could be obtained. Such an explanation—the simplest which gives exact agreement with the pressure dependence—would also provide an understanding of the apparently first order decay plot of Fig. 6. Similar arguments could be invoked to explain the more detailed evidence available for hydrocarbons.[13]

Cyanogen–Hydrogen–Oxygen Flames

Ionization in the Presence of Hydrogen. The effect of hydrogen on the ionization in cyanogen flames is different from that of any other additive, since, depending on its relative proportions it can either depress it markedly or enhance it.

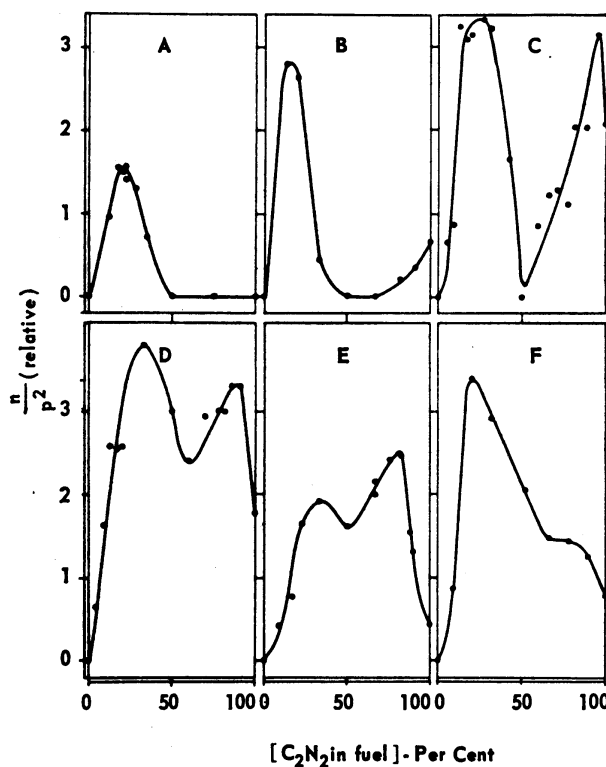The ionization in flames with hydrogen was investigated by replacing the cyanogen gradually

[C_2N_2 in fuel] - Per Cent

FIG. 7. Ionization in C_2N_2–O_2–H_2 flames, in terms of n/p^2, as a function of the percentage of cyanogen in the fuel. Curves A–E, $\lambda = 0.625, 1.0, 1.5, 2.0,$ and 4.0, respectively. Curve F, $\lambda = 1.5$, with λ redefined in terms of combustion to N_2 and CO_2.

TABLE 1

Ionization in C_2N_2-H_2—O_2 Flames (λ = 1.5)

% C_2N_2 in fuel	0	9	17	27	42	60	71	83	95	100
p, mm Hg	25	23	20	18	19	27	36	44	44	70
$n(cc^{-1}) \times 10^9$	—	6.2	17	15	7.1	8.1	22	52	80	135
$n/p \times 10^8$	—	2.7	8.5	8.3	3.7	3.0	6.1	12	18	19
$n/p^2 \times 10^7$	—	1.2	4.3	4.6	2.0	1.1	1.7	2.7	4.1	28

by hydrogen while keeping both the total unburned volume and λ constant. Plots of n/p^2 against the percentage of cyanogen in the fuel are shown in Fig. 7, A–E, for λ between 0.625 and 4.0.

Although the flames with low $[C_2N_2]$ are cooler than those with high $[C_2N_2]$, these curves should reflect the true variation in the ionization level at all points to well within a factor of two. The most outstanding feature of the curves of Fig. 6 is the appearance of a maximum (the "second ionization maximum") at about 20 per cent of cyanogen; with all other additives used n/p^2 falls continuously from the value for the pure cyanogen flame. For $0.8 < \lambda < 1.5$ addition

of only a trace of hydrogen causes a very sharp fall in n, and a rapid increase in the burning velocity of the mixture (as noted by a decrease in pressure at which the flame burns). Further addition of hydrogen produces a *rise* in n up to the second maximum—the burning velocity also goes through a maximum at that point—and then a decrease below the limit of measurement The results of a typical run are listed in Table 1

The presence of the second ionization maximum is real, and is not due to changes in the cyclotron line width—the quantity $\Delta H/p$ increases continuously as cyanogen is replaced by· hydrogen. Nor is it an effect of a play on the definition of λ, since the maximum in n/p^2 is hardly less pronounced when λ is defined in terms of combustion of the cyanogen to nitrogen and carbon dioxide, not carbon monoxide—see Fig. 7F, plotted for λ = 1.5 on the alternative definition. Figure 7F also shows that the appearance of yet another maximum in n/p^2 at high cyanogen content in oxygen-rich flames may be spurious.

These results have been plotted in terms of n/p^2 over the whole composition range, since the relationship $n \propto p^2$ is found to hold, even at the second ionization maximum. This is illustrated in Fig. 8, and suggests that the processes of ionization in cyanogen flames containing hydrogen are not analogous to those found in hydrocarbon-oxygen flames, for which $n \propto p$. The further facts that n at the second ionization maximum, in fuel-rich flames at least, is greater than the value found when the cyanogen is replaced by acetylene and that NO^+ is still the only positive ion,[8] support this view.
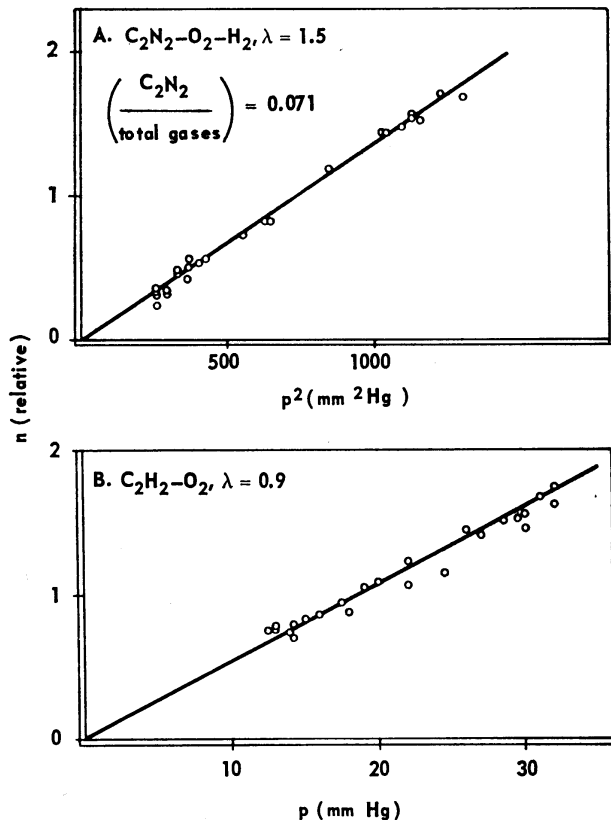
Spectral Features of Cyanogen–Hydrogen–Oxygen Flames. In the presence of hydrogen, systems due to NH, CH, and OH appear, their intensities being a function of λ and of the proportion of cyanogen in the fuel. The addition of even a trace of hydrogen reduces very markedly the intensities of the green glow, the γ–NO system, and the unidentified system in the ultraviolet, paralleling the behavior of the ionization level under the same conditions. The green glow is,

FIG. 8. A. Variation of n with p^2 in a C_2N_2-O_2-H_2 (λ = 1.5) flame. B. Variation of n with p in a C_2H_2-O_2 (λ = 0.9) flame.

however, unique in one respect. While the intensities of the above systems decay smoothly to zero as the proportion of hydrogen is increased, the glow begins to be stronger again at low $[C_2N_2]$ (20–30%) and disappears only with complete removal of cyanogen. Thus the greenish glow appears to follow n under the same conditions, at all λ and at all proportions of hydrogen.

The addition of hydrogen results in the formation of H, OH, and H_2O, because of the operation of the rapidly balanced reactions[27]

$$H_2 + O = OH + H$$

$$H_2 + OH = H_2O + H$$
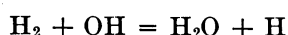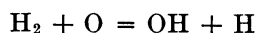
This causes a reduction in $[O]$ and lowering of the flame temperature. The pressure at which the flame burns decreases on account of the presence of new radicals through which the combustion process can proceed. These effects will, in general, be most marked in flames with less oxygen.

The production of NH can take place by, e.g.,

$$CN + OH \rightarrow CO + NH \qquad -51 \text{ kcal/mole}$$

CH can be produced by a number of reactions,

$$C_2 + OH \rightarrow CO + CH \qquad -120 \text{ kcal/mole}$$

$$C_2 + NH \rightarrow CN + CH \qquad -69 \text{ kcal/mole}$$

$$CN + NH \rightarrow N_2 + CH \qquad -32 \text{ kcal/mole}$$

The decrease of the intensities of the γ–NO system and the green glow can be explained in terms of the removal of O atoms and operation of the reaction[28]

$$NO + NH \rightarrow N_2 + OH \qquad -93 \text{ kcal/mole}$$

No satisfactory explanation of the ionization maximum observed at high $[H_2]$ can at present be put forward. The definite presence of CH in such flames makes it tempting to infer that the phenomenon arises simply through occurrence of reactions similar to those suggested to be taking place in hydrocarbon flames, viz.,

$$CH + O \rightarrow CHO^+ + e^-$$

$$CHO + H_2O \rightarrow H_3O^+ + e^-$$

$$H_3O^+ + NO \rightarrow NO^+ + H_2O + H$$
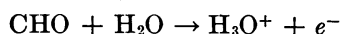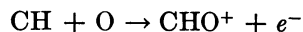
Knewstubb and Sugden[15] have suggested the third reaction to occur in hydrocarbon–oxygen systems containing added nitric oxide, and its operation could explain the limitation of the positive ion spectrum to NO^+. There are puzzling features of the phenomenon, however, such as the pressure dependence, which do not seem to fit with such a simple explanation. It is hoped that further insight may be provided by a quantitative photometric study of the spectral features described, and this is currently being undertaken.

REFERENCES

1. BAKER, M. R. and VALLEE, B. L.: J. Opt. Soc. Am. *45*, 773 (1955).
2. THOMAS, N., GAYDON, A. G., and BREWER, L.: J. Chem. Phys. *20*, 369 (1952).
3. JAMES, H.: Rev. Inst. Franc. Petrole et Ann. Combustibles Liquides *13*, 83 (1958).
4. ROBERTSON, N. C. and PEASE, R. N.: J. Am. Chem. Soc. *64*, 1880 (1942).
5. JENNINGS, K. R. and LINNETT, J. W.: Trans. Faraday Soc. *56*, 1737 (1960).
6. BASS, A. M. and BROIDA, H. P.: J. Mol. Spectroscopy *2*, 42 (1958).
7. NICHOLLS, R. W. and KRISHNAMAHARI, S. L. N. G.: Can. J. Chem. *38*, 1652 (1960).
8. VAN TIGGELEN, A.: Private communication, Univ. de Louvain, Belgium, 1960.
9. CALCOTE, H. F.: Combustion and Flame *1*, 385 (1957).
10. GAYDON, A. G. and WOLFHARD, H. G.: Flames. Chapman and Hall, 1953.
11. BULEWICZ, E. M.: J. Chem. Phys. *36*, 385 (1962).
12. BULEWICZ, E. M. and PADLEY, P. J.: J. Chem. Phys. *35*, 1590 (1961).
13. BULEWICZ, E. M. and PADLEY, P. J.: This volume, p. 638.
14. BULEWICZ, E. M. and PADLEY, P. J.: Unpublished data, 1961.
15. KNEWSTUBB, P. F. and SUGDEN, T. M.: Proc. Roy. Soc. (London) *A255*, 520 (1960).
16. KNEWSTUBB, P. F. and SUGDEN, T. M.: *Seventh Symposium (International) on Combustion*, p. 247. Butterworths, 1958.
17. DE JAEGARE, S., DECKERS, J., and VAN TIGGELEN, A.: *Eighth Symposium (International) on Combustion*, p. 155. Williams and Wilkins, 1962.
18. KOHN, H.: Private communication, Duke University, Durham, N.C., 1960.
19. PADLEY, P. J. and SUGDEN, T. M.: *Eighth Symposium (International) on Combustion*, p. 164. Williams and Wilkins, 1962.
20. WILLIAMS, H.: *Eighth Symposium (International) on Combustion*, p. 179. Williams and Wilkins, 1962.

21. Calcote, H. F.: *Eighth Symposium* (*International*) *on Combustion*, p. 184. Williams and Wilkins, 1962.
22. Gaydon, A. G.: *The Spectroscopy of Flames.* John Wiley and Sons, 1957.
23. Ultee, C. J.: J. Phys. Chem. *64*, 1873 (1960).
24. Broida, H. P. and Tanaka, I.: J. Chem. Phys. *36*, 236 (1962).
25. Kaufman, F.: J. Chem. Phys. *28*, 992 (1958).
26. Doering, J. P. and Mahan, B. H.: J. Chem. Phys. *36*, 569 (1962).
27. Bulewicz, E. M., James, C. G., and Sugden, T. M.: Proc. Roy. Soc. (London) *A235*, 89 (1956).
28. Bulewicz, E. M. and Sugden, T. M.: Unpublished data, 1958.

Discussion

Dr. E. P. Gray (*APL/The Johns Hopkins University*): The comments which I want to make on the paper of Dr. Bulewicz and Dr. Padley, are concerned solely with the limitations inherent in, and the care required in using the cyclotron resonance method for probing the plasma constituting a flame; I shall not discuss the mechanism and chemistry of the flames inferred from the measured quantities, namely the average electron concentration and the collision frequency.

The main object of these comments is to point out that special care is required to keep the electron concentration of the flame being probed very low. Failure to do so will result in a broadening of the cyclotron resonance line by a mechanism unrelated to collision broadening, so that the collision frequency and the electron concentration are not obtainable from the line width. However, before proceeding any further I want to stress that the authors of this paper did take the requisite care, and that their results can not be criticized on those grounds. What I want to accomplish is to show how severe the requirements are, so as to help others who might want to use this method to avoid this trap.

The theory for the line width in terms of the collision frequency, upon which the interpretation of the measurements depends, was developed by Kelly, Margenau, and Brown[1] for resonance absorption by a *single particle* in a magnetic field. Only when the circular plasma frequency, $\omega_p = (4\pi n e^2/m)^{\frac{1}{2}}$ (where n is the electron concentration, e the electronic charge, and m the electron mass) is sufficiently smaller than the circular cyclotron frequency, $\omega_c = eB/mc$ (where B is the magnetic field and c, the velocity of light), is this single particle theory applicable.

An exact theory for cyclotron resonance absorption, which is valid even if $\omega_p > \omega_c$, has been developed by Buchsbaum, Mowrer, and Brown.[2] They compute the complex frequency shift, $\Delta f/f$, of the resonant frequencies of a cylindrical cavity filled with a uniform plasma subjected to an external axial magnetic field. The imaginary part of Δf is directly related to the real part of the transverse conductivity, and therefore to the line shape. Their calculation for the TE_{011} resonance is qualitatively applicable to Bulewicz and Padley's experiments, in that for both cases the external magnetic field, the direction of propagation of the microwaves, and the electric field vector are mutually perpendicular. The difference in geometry between the computed case of the cylindrical cavity and the actual experimental situation will make an accurate numerical comparison impossible, but should not affect the order of magnitude of the quantities involved.

The theory predicts that the complex frequency shift for the TE_{011} resonance is given by

$$\frac{\Delta f}{f} = \frac{x_{01}^2 (R/a)^4}{16 J_0^2(x_{01})} \alpha^2 \left\{ \frac{[(1 - \alpha^2)(1 - \alpha^2 - \beta^2) + \gamma^2] + j\gamma[(1 - \alpha^2)^2 + \beta^2 + \gamma^2]}{(1 - \beta^2 - \gamma^2 - \alpha^2)^2 + \gamma^2(2 - \alpha^2)^2} \right\},$$

where $x_{01} = 3.832$, the first root of $J_1(x) = 0$; R is the radius of the (uniform) plasma column; a is the radius of the cavity; $\alpha = \omega_p/\omega$; $\beta = \omega_c/\omega$; $\gamma = \nu/\omega$; ν is the collision frequency; and ω is the (circular) microwave frequency. From the imaginary part of $\Delta f/f$ the cyclotron resonance absorption has been obtained. This is shown in Fig. 1a, with the parameter $\nu/\omega = 0.01$, very close to the value of 0.015 used in Bulewicz and Padley's experiment. The most striking feature is a shift of the resonant frequency from $\omega = \omega_c$ to a new value, $\omega = (\omega_c^2 + \omega_p^2)^{\frac{1}{2}}$, but with a line width which does not change markedly until ω_p approaches ω. This phenomenon is caused by the absorption associated with an anomalous dispersion of the real part of $\Delta f/f$ (i.e., of the index of refraction), which has also been noted by Bulewicz and Padley.[3] If the plasma were uniform, therefore, the electron concentration and collision frequency could be obtained from the line width even for relatively large values of ω_p.

For the highly nonuniform plasma actually used, however, this conclusion changes drastically. In that case the observed line can be considered as an appropriate average over a group of these lines
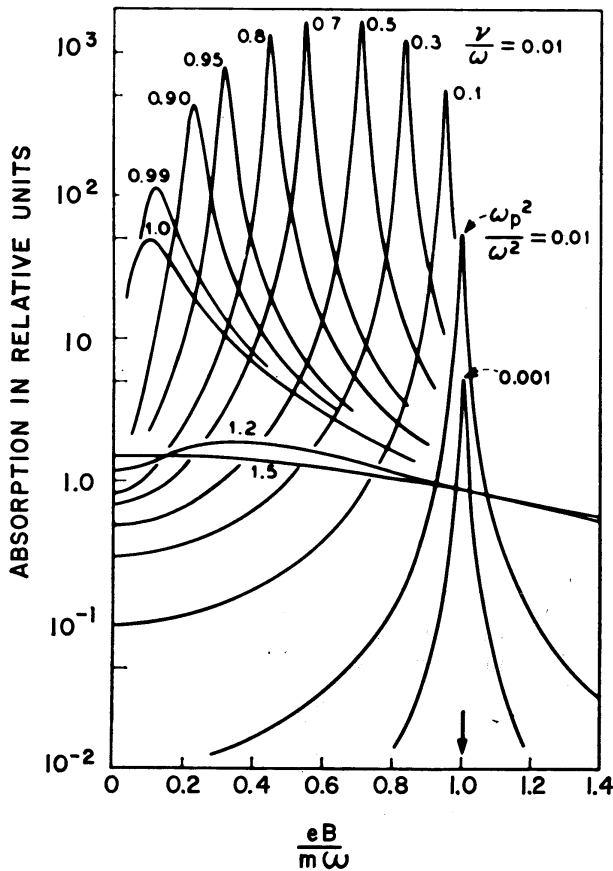
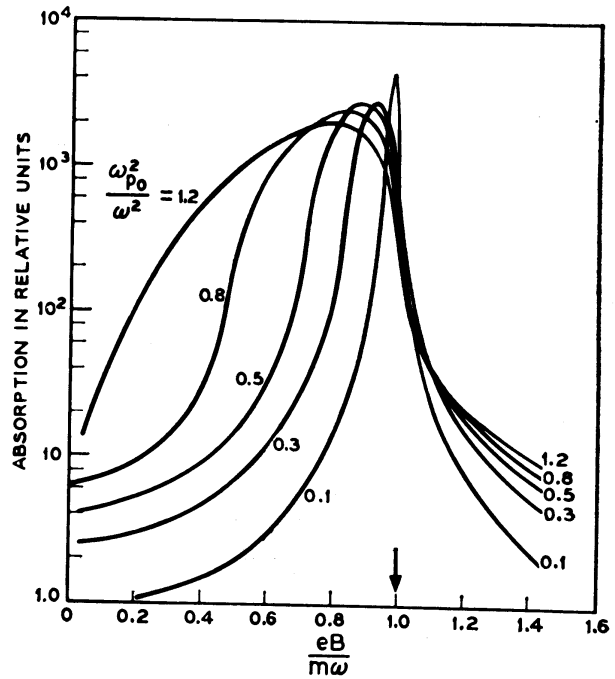FIG. 1a. Absorption vs. magnetic field in a uniform plasma.

FIG. 1b. Absorption vs. magnetic field in a non-uniform plasma.

computed for the uniform plasma. Since each of these lines peaks at a different cyclotron frequency, the average will have a width that is governed by this frequency shift and not by the collision broadening which governs the width of the individual lines. The result of this averaging is shown in Fig. 1b, where the average has been computed over a
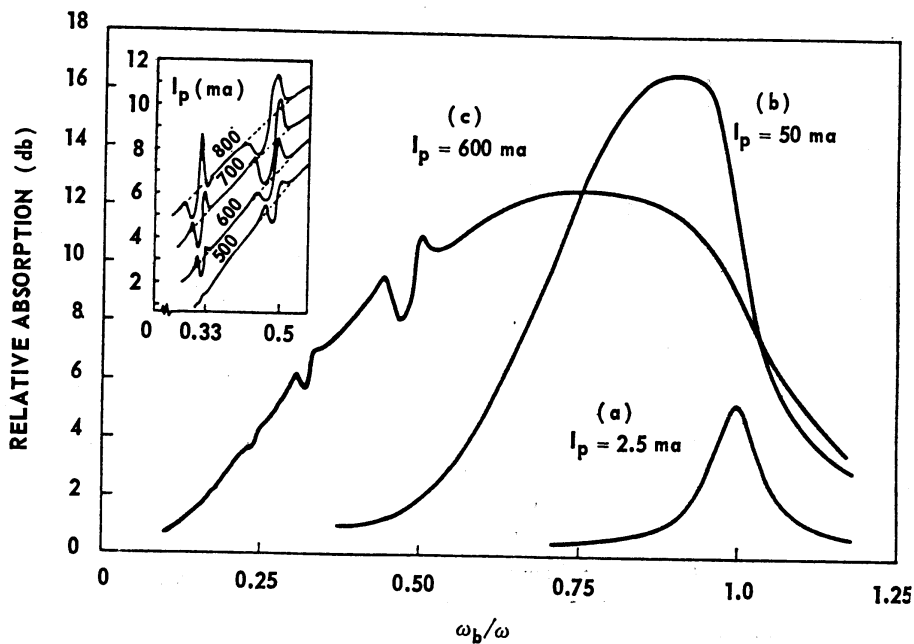

FIG. 2. Microwave power absorption in a cavity-plasma system as a function of magnetic field. The plasma is the positive column of a helium discharge at a pressure of 0.5 mm Hg.

plasma profile of the form $n/n_{max} = 1 - r^2/R^2$, where R is the radius of the plasma column. The values of ω_p shown correspond to the electron concentration on the axis. It is evident, therefore, that $\omega_p{}^2/\omega^2$ must be considerably below 0.1, the lowest value shown, in order that the line width be due to collision broadening. A sensible criterion would appear to be the requirement that the real part of the (circular) frequency shift, $\Delta\omega_c$, be considerably less than the line width. Such a criterion leads to the requirement that

$$(\omega_p/\omega)^2 \ll 4\nu/\omega.$$

These calculations have been confirmed experimentally by Bekefi, Coccoli, Hooper, and Buchsbaum.[4] Figure 2 shows the cyclotron absorption line for three different values of the current (corresponding to different ω_p). For case (b), $\omega_p{}^2/\omega^2$ is roughly 0.2, and the line is evidently broadened. For case (c), $\omega_p{}^2/\omega^2$ is about 0.01, and no broadening is evident. (I do not know the value of ν/ω, except that it lies between 10^{-4} and 10^{-1}.) These cases bracket the regime where noncollisional broadening could be troublesome.

In Bulewicz and Padley's experiment this restriction has been observed. For the highest value of electron concentration they mention, namely 5×10^{10} per cm³, the parameter $\omega_p{}^2/\omega^2$ is approximately 0.002, as compared to a value for $4\nu/\omega$ of about 0.06. Their line widths, therefore, may certainly be interpreted on the basis of collision broadening.

In conclusion, I want to note that the qualitative features of this anomalous dispersion, and its effect on the asymmetry of the resonance line, have been pointed out previously by Bulewicz and Padley.[3] Only the application of Buchsbaum, Mowrer, and Brown's[2] detailed numerical calculations to the cyclotron resonance probing of flames is new. I also wish to acknowledge several useful conversations with Dr. Buchsbaum, and to thank him for providing me with a copy of some of his computed curves.

DR. P. F. KNEWSTUBB (University of Cambridge): In connection with the results shown in Fig. 7 of the paper by Bulewicz and Padley, I feel that it may be of interest to present a brief account of some measurements relating to the ionization of nitric oxide in flames. A premixed flame of acetylene-oxygen-nitrogen was formed, and 1% by volume of nitric oxide added to the mixture. The concentration of nitric oxide ion, measured by the mass spectrometer was found to reach a large maximum value just above the reaction zone, falling to lower values upstream, but to be everywhere many times greater than the level expected for thermal ionization. This, coupled with the rapid variation with distance, convinces us that the ion is produced by chemi-ionization. The observation that addition of nitric oxide causes also a large reduction of H_3O^+ ion concentra-

tion suggests strongly that the NO^+ is derived from the same source of chemical energy, at the expense of H_3O^+.

Accepting the scheme of chemi-ionization which is proposed by three papers in this Symposium, we may consider the interfering effect of nitric oxide in possible change exchange reactions:

$$CHO^+ + NO \rightarrow NO^+ + CHO \qquad (1)$$

$$H_3O^+ + NO \rightarrow NO^+ + H_2O + H. \qquad (2)$$
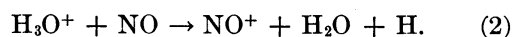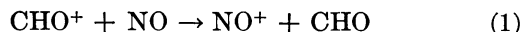
Examination of the quantities involved suggests that reaction (1) is unlikely to compete so successfully with the proton transfer reaction (3) as to produce the observed results

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO. \qquad (3)$$

A suggestion of the importance of reaction (2) with which we are credited towards the end of this paper, was, I believe, made at a time when a high value of the heat of formation of H_3O^+ (of about 195 kcal/mole) seemed tenable. As a result of work published in the interim, a much lower value (of about 137 kcal/mole) is now favored for this quantity, and we would no longer support reaction (2) as likely to produce NO^+.

One suggestion may be made which seems to fit well all tests which we have been able to apply, as follows:

$$H + NO + M \rightarrow HNO + M \qquad (4)$$

$$HNO + H_3O \rightarrow NO^+H_2 + H_2O \qquad (5)$$
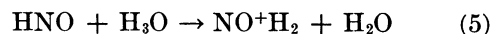
Details of the arguments leading to this will be given elsewhere. A scheme of this type, with the additional parameters thereby introduced, might be able to explain the results portrayed in Dr. Padley's Fig. 7.

DR. P. J. PADLEY (University of Cambridge): A priori, a scheme along the lines suggested by Dr. Knewstubb appears to be highly plausible: for example, it gives a qualitative explanation of the shape of our Fig. 7. However, as we have pointed out, any such scheme involving "reactions similar to those taking place in hydrocarbon flames," i.e., where the primary ionization step is bimolecular, does not escape the difficulty presented by the pressure-dependence of the electron concentration in cyanogen–oxygen–hydrogen flames; the scheme of ion production must, apparently, involve a termolecular reaction, as in flames from which hydrogen is absent.

So far we have only thought of one mechanism satisfying this requirement and one, indeed, involving HNO, in an ion-producing scheme. This species, highly likely to be present in such flames and not, of course, present in pure cyanogen-oxygen flames
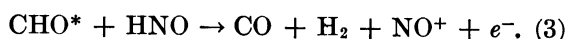
seems to be produced by a three-body reaction

$$H + NO + X \rightarrow HNO + X, \qquad (1)$$

where X is a third body. If this were to react with CHO* (vibrationally and electronically excited CHO), produced as an intermediate in the reaction

$$CH + O \rightarrow [CHO^*] \rightarrow CHO^+ + e^-, \qquad (2)$$
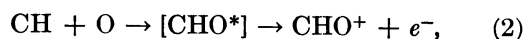
then ions could be produced by

$$CHO^* + HNO \rightarrow CO + H_2 + NO^+ + e^-. \qquad (3)$$

Such a scheme would be about 5 kcal/mole exothermic. We have already suggested (our paper, this Symposium) that a reaction of type (3), *viz.*,

$$CHO^* + M \rightarrow CO + H + M^*,$$
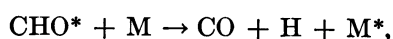
where M is an electronically excited metal atom, appears to satisfy well all observations so far made on metal atoms in the reaction zones of such flames. However, this scheme, (1)–(3), requires an almost impossibly high concentration of CHO* and will fail if reaction (2) is faster than reaction (3); thus we had not proposed it in our paper.

DR. A. FONTIJN (*AeroChem Research Laboratories*): Could Dr. Padley elaborate on the reasons why acetylene flames have a higher degree of ionization than the other flames studied?

DR. P. J. PADLEY: Comparing various hydrocarbon fuels, it appears quite possible that both [CH] and [O] could increase slightly as the hydrogen-to-carbon ratio decreases, whether or not there is a change in the degree of unsaturation in the original molecule. In C_2H_2–O_2 flames, for example, a smaller proportion of the combustion steps will involve processes similar to those in H_2–O_2 combustion than in, say, CH_4–O_2 flames, and this may well cause [O] to be higher. Again, the more hydrogen atom stripping that is necessary to produce CH from the original molecule, the later in the combustion is ionization likely to take place. This would certainly explain the slight upward curvature of the saturated hydrocarbons' plot. The picture is not necessarily complicated by the observation that the EF value for benzene is not three times that for acetylene.

The extraordinary behavior of the EF values for the acetylenic series would also be intelligible on this basis, when it is remembered that, from our results for mixed fuels, the presence of the CH bond in the original molecule appears to be a necessary condition for the production of ions by the CH + O mechanism. Methyl acetylene is the first member of the series to contain a carbon atom which does not make a CH bond; therefore, the EF value for this molecule can certainly be no greater than that for acetylene itself (the same should be true for allene, when compared to ethylene). In fact, it is observed

to be somewhat less, which can be interpreted in terms of the slightly different over-all carbon to hydrogen ratios in these two molecules. From methyl acetylene onwards the series proceeds "normally," i.e., the increment in EF for each additional carbon atom is, to a good approximation, the same as for other hydrocarbons into which an additional CH group is introduced.

Those who have remarked on parallels between CH emission and degree of ionization (e.g., Professor Kistiakowsky's shock tube studies) may be oversimplifying the issue if such observations are suggested to support the CH + O $\rightarrow$ CHO$^+$ + e^- ionization mechanism. For if traces of various hydrocarbons are introduced into hydrogen–oxygen–nitrogen flames, the CH emission intensity is found only in isolated cases (e.g., benzene and acetylene) to be approximately proportional to the fuel concentration; for most fuels a power dependence between 1.5 and 3.0 is observed. Since the proposed ionization mechanism requires CH ground state to be proportional to the fuel concentration, at least some CH emission must arise by processes other than by excitation of the ground state CH.

There are two important consequences of our observation that the electron concentration in hydrocarbon–oxygen flames is proportional to the pressure:

1. It is highly unlikely that the forward ionization step involves a third body. *A priori* the electrons could be produced in either a bimolecular or termolecular process; they could be destroyed by direct recombination with positive ion (either with or without a third body), by electron attachment or by diffusion to the walls. Thus eight simple steady state equations for the electron concentration can be set up, and of these only two satisfy the pressure dependence observation: termolecular electron production coupled with termolecular destruction, or bimolecular production coupled with bimolecular destruction. Now the recombination constant measured with positive ions, at 2×10^{-7} cm^3 sec^{-1} (King; Calcote; Green and Sugden; *vide* this Symposium) is rather fast for a termolecular process, and the fact that this recombination constant does not increase as the pressure decreases points to a bimolecular recombination process. Therefore the forward step, producing the ions, will be bimolecular.

2. Electron attachment is indicated as responsible for electron removal in our low-pressure system. Diffusion processes would imply an electron concentration proportional to the cube of the pressure, and seem therefore to be eliminated. A second order (in ions) recombination process is eliminated since this would predict the electron concentration proportional to the square root of the CH, or fuel, concentration, whereas our results indicate a direct proportionality. Thus one is only left with a bi-

molecular, first order (in electrons) process to consider, and this corresponds to electron attachment. It is perhaps significant that a similar analysis of the cyanogen-oxygen system, for which we observe a quite different pressure-dependence of the electron concentration, also leads to the same conclusion.

Thus in hydrocarbon-oxygen flames the recombination step could be

$$H_3O^+ + OH^- \rightarrow \text{products}$$
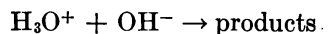
with the OH^- produced by electron attachment, and in cyanogen–oxygen flames,

$$NO^+ + CN^- \rightarrow N_2 + CO$$
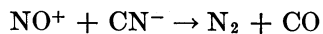
with the CN^- produced by electron attachment. A slightly puzzling point is that our results imply the concentration of the attaching species not to vary significantly with flame composition, contrary to expectations. A more detailed answer must await the results of future work.

REFERENCES

1. KELLY, D. C., MARGENAU, H., and BROWN, S. C.: Phys. Rev. *108*, 1367 (1957).
2. BUCHSBAUM, S. J., MOWRER, L., and BROWN, S. C.: Phys. Fluids *3*, 806 (1960).
3. BULEWICZ, E. M. and PADLEY, P. J.: J. Chem. Phys. *35*, 1590 (1961).
4. BEKEFI, G., COCCOLI, J. D., HOOPER, E. B., and BUCHSBAUM, S. J.: Phys. Rev. Letters *9*, 6 (1962).